

Thermotropic Comblike Polymers with Lipobiphenyl Side Chains: Factors Governing Nature of Mesophases

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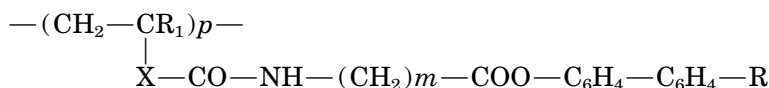
ABSTRACT: In this article we describe the thermotropic behavior of comblike polymers with three types of main chains (polyacrylamide, polymethacrylamide, and polystyrylamide), two lengths of spacers (10 or five methylene groups), and three types of mesogenic cores (biphenyl, carbonitrilbiphenyl, and 2-methyl-1-butoxybiphenyl). The spacers are always linked to the mesogens by an ester bond. All the polymers are smectic at room temperature and exhibit two different smectic phases as a function of temperature, except for the polymer with a styrylamide main chain and a carbonitrilbiphenyl mesogen that presents only one mesophase; but the type of smectic phases is governed by the nature of both the main chain and the substituent R of the biphenyl core. Polyacrylamide polymers exhibit only bilayer smectic phases whose type is determined by the nature of the substituent R of the biphenyl; the smectic phases are SI2 and SC2 for R = H, SC2 and SA2 for R = CN, and SF2 and SC2 for R = O—CH₂—CH(CH₃)—C₂H₅. On the contrary, polymethacrylamide and polystyrylamide polymers exhibit two perpendicular monolayer smectic phases, SB1 and SA1, except for R = CN where a SAd phase replaces the SA1 phase. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 2407–2417, 1997

Key words: comblike polymers; lipobiphenyl side chains; thermotropic properties; X-ray diffraction; mesomorphic structures

INTRODUCTION

Some years ago we showed that comblike polymers with polyacrylamide or polymethacrylamide main chains and lipopeptidic^{1–3} or liposaccharidic⁴ side chains exhibit both thermotropic and lyotropic properties. So it was interesting to see by replacing lipopeptides and liposaccharides by li-

pobiphenyls, if the polyacrylamide polymers would still be able to exhibit liquid-crystalline properties. To verify that hypothesis we undertook the synthesis of comblike polymers with: polyacrylamide,^{5,6} polymethacrylamide,⁷ and polystyrylamide⁸ main chains; spacers with five and 10 methylene groups; and three different biphenyl derivatives as mesogens. All these polymers can be described by the general formula:



with R₁ = H or CH₃, X = — or C₆H₄, m = 5 or 10, and R = H or CN or O—CH₂—CH(CH₃)—C₂H₅.

In the present article we illustrate the synthesis, macromolecular characterization, and deter-

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Table I Nomenclature of Monomers and Polymers Studied

Monomer	Polymer	R ₁	X	m	R
IIIa	pIIIa	H	—	10	H
IIIb	pIIIb	H	—	10	CN
IIIc	pIIIc	H	—	10	O—CH ₂ —CH(CH ₃)—C ₂ H ₅
III d	pIII d	CH ₃	—	10	H
III e	pIII e	CH ₃	—	10	CN
III f	pIII f	H	—	5	O—CH ₂ —CH(CH ₃)—C ₂ H ₅
IV b	pIV b	H	C ₆ H ₄	10	CN
IV c	pIV c	H	C ₆ H ₄	10	O—CH ₂ —CH(CH ₃)—C ₂ H ₅

mination of the thermotropic behavior of the three families of comblike polymers (Table I), using the example of polymers pIIIe and pIII f. Then we show the respective influence of the main factors governing the nature and the geometrical parameters of the mesophases. These factors are the nature of the main chains, the length of the spacers, the nature of the substituant R of the biphenyl, and the temperature.

EXPERIMENTAL

Materials

Dicyclohexylcarbodiimide (DCC), *N*-hydroxysuccinimide (HOSu), pyrrolidinopyridine (PPY), 11-aminoundecanoic acid, 4-hydroxybiphenyl, and 4'-hydroxy-4-biphenylcarbonitrile from Aldrich, and 4-vinylbenzoic acid from Lancaster were used as received. Acryloylchloride and methacryloylchloride from Aldrich were distilled under a vacuum to eliminate inhibitors, α, α' -Azobisisobutyronitrile (AIBN, 99% pure from Merck) was recrystallized before use. Solvents were purified by classical methods.

Synthesis of Monomers

11-Methacryloylamidoundecanoic acid (**II**), 11-acryloylamidoundecanoic acid (**II**), and 11-styrylamidoundecanoic acid (**III'**) were synthesized as already described.^{4,6,8} 6-Acryloylamidohexanoic acid was derived by dissolving 11 g (196 mmol) of KOH in 100 mL water, then 6.7 g (50 mmol) of 6-aminohexanoic acid (**I**) were added and the solution was cooled to 0°C. Then 7.5 mL (75 mmol) of acryloylchloride were added dropwise under agitation. After 4 h of reaction at 0°C, 1N HCl was added until pH 2 was obtained. The precipitate formed was filtrated, washed with cold

HCl, and dried under a vacuum. The product was purified by extraction with ethanol (yield 54%).

Monomers **IIIa**, **IIIb**, **IIIc**, **III d**, **IV b**, and **IV c**, were synthesized as described in the literature.⁵⁻⁸

Monomer **III e** was formed by dissolving 5.4 g (20 mmol) of 11-methacryloylamidoundecanoic acid (**II**) in 100 mL of dry CH₂Cl₂ under an inert atmosphere and degassing; then 4.02 g (20 mmol) of 4'-hydroxy-4-biphenylcarbonitrile and 3.02 g (20 mmol) of PPY were added. The solution was cooled to 0°C and 4.16 g (20 mmol) of DCC in solution in 20 mL CH₂Cl₂ were added dropwise. After 20 min at 0°C and 68 h at room temperature, the solution was filtered off to eliminate the precipitate of DCU; the filtrate was washed at first with 0.5N HCl and then with saturated NaHCO₃; the organic solution was dried on MgSO₄ and evaporated. The monomer was recrystallized in acetonitrile at 64°C; the precipitate obtained by cooling was filtered off, washed with acetonitrile, and dried under a vacuum (yield 58%). TLC: R_f = 0.37; eluant: AcOEt/C₆H₁₂/CHCl₃ (3/3/5). FTIR (Nicolet 20SX) (cm⁻¹): 3295, 1653, 1542 (amide); 2921, 2851 (aliphatic chain); 1748 (ester); 1625 (vinyl); 2227 (C=N). ¹H-NMR spectra at 250 MHz (CDCl₃, TMS) is given in Figure 1, and ¹³C-NMR spectra at 62.9 MHz (CDCl₃) is given in Figure 2.

Monomer **III f** was prepared in the same way as **III e** with a yield of 68% from 3.5 g (20 mmol) of 6-acryloylamidohexanoic acid (**II**) and 5.12 g (20 mmol) of 4-hydroxy(4'(2-methyl)butyloxy)-biphenyl, except that THF replaced CH₂Cl₂ as the reaction solvent. FTIR (cm⁻¹): 3301, 1655, 1542 (amide); 2920, 2850 (aliphatic chain); 1745 (ester); 1624 (vinyl). ¹H-NMR, 250 MHz (MeOD, TMS) (ppm): 7.6–6.9 (H aromatic); 6.2 (=CH₂); 5.6 (=CH); 3.25 (H₁); 2.3 (H₅); 1.6 (H₂, H₄); 1.35 (H₃).

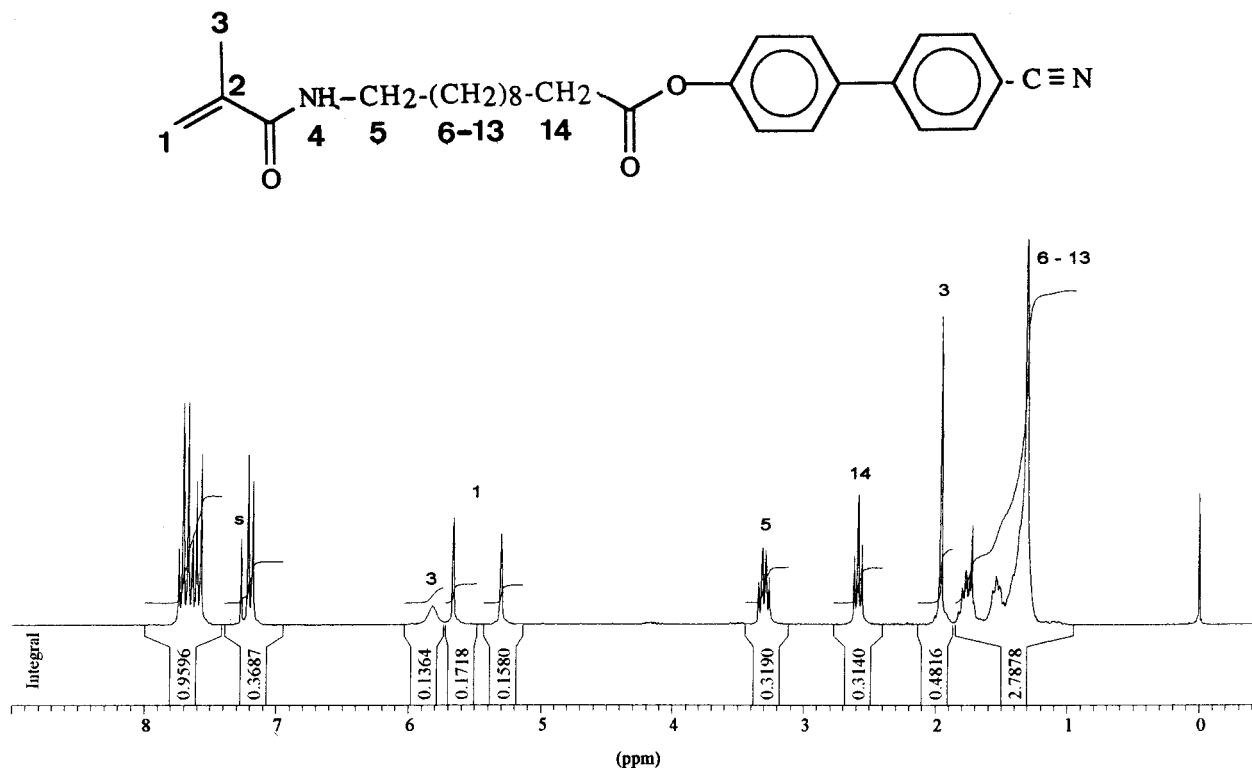


Figure 1 $^1\text{H-NMR}$ spectra of the monomer **IIIe**.

Polymerization

Polymerization under Argon

Two grams of monomer **IIIe** were solubilized in 10 mL THF and degassed under argon, then 0.05 g of AIBN was added. The solution was maintained at 65°C for 150 h under argon and agitation. Several samples were taken at various reaction times and injected in GPC columns and the degree of conversion was deduced from the surface areas of the monomer and polymer.⁷ The polymer **pIIIe** was recovered by precipitation in methanol.

Polymerization under Vacuum

Two grams of monomer **IIIe** were solubilized in 10 mL chloroform; 0.05 g of AIBN was added and the solution was degassed under a vacuum. The solution was maintained at 65°C for 150 h under a vacuum and agitation. The polymer **pIIIe** was recovered by precipitation in methanol.

Characterization of Polymers

Polymers were characterized by $^1\text{H-NMR}$ at 250 MHz (CDCl_3 , TMS) (ppm): 1.3 (m, 16H); 2.6 (t, 2H); 3.3 (m, 2H); 7.1, 7.4, 7.6 (m, 9H, aromatic).

The molecular characteristics of the polymers (M_n , M_w , and M_w/M_n) were determined by light scattering (Brookhaven) in THF or chloroform and GPC in THF (PSS gel mixed b columns) using polystyrene calibration (Table II).

X-Ray Diffraction

X-ray diffraction experiments were performed on unoriented samples with two types of cameras: a Guinier-type camera and a pinhole camera.

The Guinier-type focusing camera, operated under a vacuum, was equipped with a bent quartz monochromator (reflection 101), giving a linear collimation of strictly monochromatic X rays ($\text{Cu K}\alpha_1$, $\lambda = 1.54 \text{ \AA}$), and a device for recording the diffraction patterns from samples at various temperatures between 20 and 200°C with an accuracy of 1°C.

The pinhole camera was specially designed in the laboratory to operate with capillaries containing powder or oriented samples, under a vacuum, with an Ni filtrated Cu beam ($\lambda = 1.54 \text{ \AA}$). It was equipped with the same heating device as the Guinier camera.

Several exposures were made to measure the

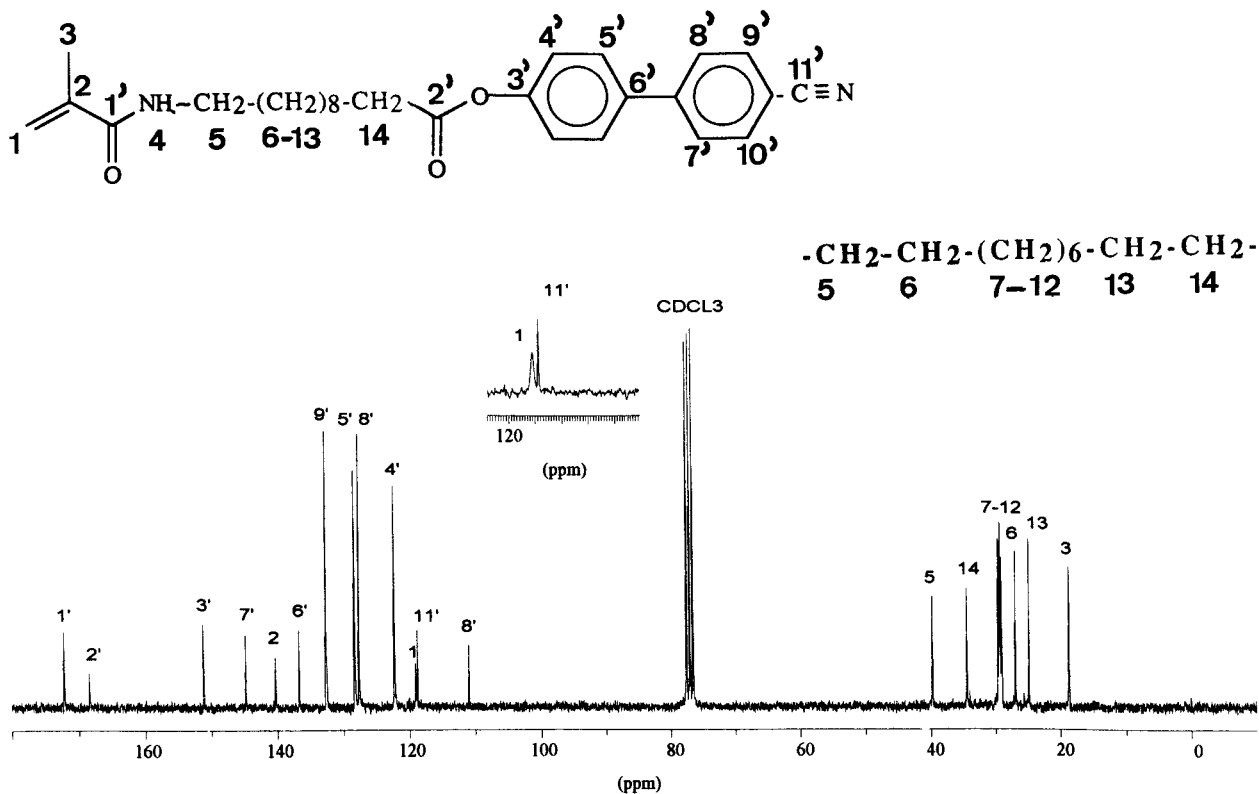


Figure 2 ^{13}C -NMR spectra of the monomer **IIIe**.

strongest and the weakest reflections. Intensities of the reflections were measured with a laboratory built microdensitometer specially designed to analyze X-ray diagrams provided by linear focusing and pinhole cameras. Experimental amplitudes of diffraction of the different orders of reflections on the smectic layers were corrected for the Lorentz polarization factor⁹ and were normalized so that the strongest one had an amplitude of one. For the polymer **pIIIc** for instance, the values found were $a_1 = 1$, $a_2 = 0.38$, and $a_3 = 0.72$ for the first mesophase and $a_1 = 1$, $a_2 = 0.36$, and $a_3 = 0.74$ for the second mesophase.

RESULTS

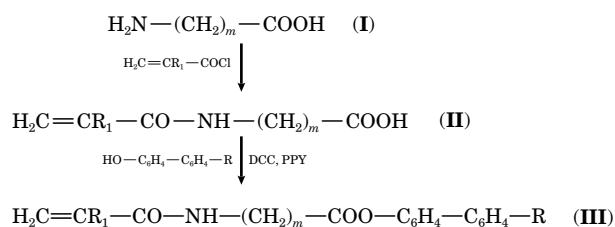
Synthesis of Polymers

The preparation of all polymers involves two steps: synthesis of a polymerizable biphenyl derivative from an α,ω -aliphatic amino acid by fixation at the amine end of the polymerizable group and at the carboxylic acid end of the biphenyl mesogenic group, followed by the transformation of this

monomer into a comblike polymer by radical polymerization.

The number of steps (two or three) necessary to prepare the monomers depends upon the nature of the main chain.

The acryl- and methacrylamidoalkanoylbiphenyl derivatives were synthesized in two steps:



In the first step, 11-aminoundecanoic acid (**I**) was transformed into the polymerizable acid (**II**) upon nucleophilic substitution between acryloyl or methacryloyl chloride and its amino group in aqueous solution at basic pH.

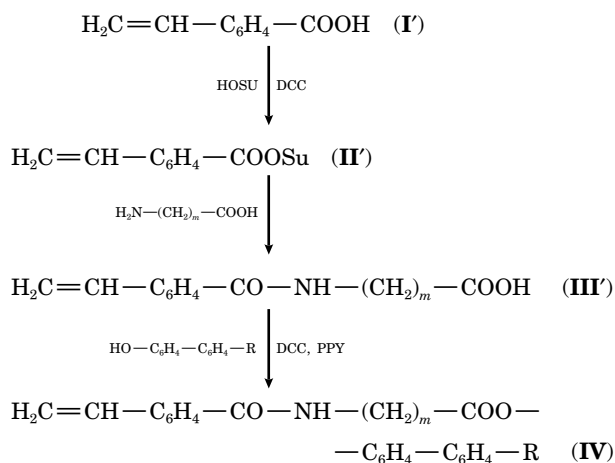
In the second step, the polymerizable acid (**II**) was esterified by the 4-hydroxybiphenyl derivative in the presence of the coupling agent DCC and the PPY that forms *N*-acylpyridinium salts

Table II Molecular Characteristics of Polymers Studied

Polymer	M_n	M_w	M_w/M_n
pIIIa	24,500	42,300	1.73
pIIIb	73,100	94,300	1.29
pIIIc	29,000	42,700	1.47
pIIId	19,700	24,000	1.22
pIIIe	15,100	30,200	2.00
pIIIf	29,000	36,600	1.26
pIVb	26,700	49,700	1.86
pIVc	26,700	31,000	1.37

that are more electrophilic and increase both the reaction speed and the reaction yield.^{10,11}

The styrylamidoundecanoylbiphenyl derivatives were synthesized in three steps:



In the first step, the 4-vinylbenzoic acid is activated under the form of its succinimidyl ester (**II'**) by action of a nucleophilic agent (HOSu) and a coupling agent (DCC).

In the second step the active ester (**II'**) is aminolysed by the 11-aminoundecanoic acid to give the styrylamidoundecanoic acid (**III'**).

In the third step the styrylamidoundecanoic acid (**III'**) is esterified by the 4'-hydroxybiphenyl derivative in the presence of DCC and PPY to give the styrylamidoundecanoylbiphenyl derivative (**IV**).

The polymerization of monomers **III** and **IV** was carried out with AIBN initiator at 65°C by two methods: under a vacuum in chloroform solution, and under argon in a THF solution to allow the measurement of the degree of conversion of the monomer as a function of time.

Polymerization kinetics were followed by two methods: ¹H-NMR and GPC.⁵⁻⁸ Figure 3 gives the

variation of the conversion versus time for the polymer pIIIe and shows that the conversion is higher than 90% after 160 h of polymerization.

Determination of Structure of Mesophases

To illustrate the method of determination of the structure of the polymer mesophases and their thermotropic behavior, we use the examples of polymer **pIIIb** with a polyacrylamide main chain, a spacer with five methylenes, and a 2-methylbutoxybiphenyl mesogen, and polymer pIIIe with a polymethacrylamide main chain, a spacer with 10 methylenes, and a carbonitrilbiphenyl mesogen.

Polymer pIIIb: $R_1 = \text{H}$, $m = 5$,
 $R = \text{O}-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{C}_2\text{H}_5$

All X-ray patterns recorded at temperatures between room and isotropization temperatures exhibited three sharp reflections in the low angle domain and a sharp reflection (Fig. 4) or a diffuse band (Fig. 5) in the wide angle domain, depending upon the temperature.

The low angle reflections can be indexed as the 001 reflections of a lamellar structure. The wide angle reflection at 5.5 Å (Fig. 4) is characteristic of a smectic structure with hexagonal packing of the side chains (smectic B, F, or I).¹² The wide angle band at 5.0 Å (Fig. 5) is characteristic of a disordered smectic structure (smectic A or C).¹²

To make a choice between the possible smectic structures, we compared the thickness d of the

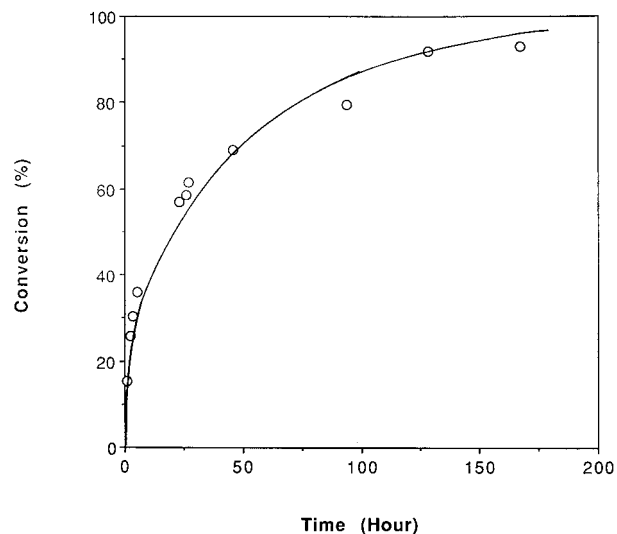


Figure 3 Conversion–time curve of the polymerization under argon in THF solution of the monomer **IIIe**.

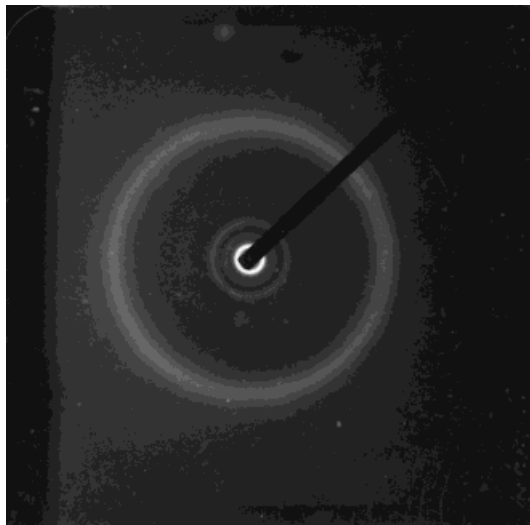


Figure 4 Pinhole camera powder X-ray diagram of the SF2 mesophase of the polymer **pIIIIf** at 70°C, showing the three small angle sharp reflections and the wide angle sharp reflection.

smectic layers ($d = 49.0$ Å for the first mesophase and $d = 47.8$ Å for the second mesophase) with the length $L = 27.4$ Å of the repeating unit of the polymer (corresponding to a monolayer structure) and the length $2l + p = 50.8$ Å of two side chains and one main chain (corresponding to a bilayer structure) measured on CPK models with the spacer in an all trans configuration. Because d is much higher than L but smaller than $2l + p$, the smectic structures can be double layer smectic structures (F2 or I2 or C2) [Fig. 6(a)] with an angle of tilt ϕ given by $\cos \phi = d/(2l + p)$ or interdigitated perpendicular smectic structures (Bd or Ad) [Fig. 6(b)].

To distinguish tilted smectic structures from perpendicular smectic structures, we derived intensity profiles $\rho(z)$ along the direction z perpendicular to the smectic planes from the intensities of the low angle reflections of X-ray diagrams.⁵

Taking into account the symmetry of the structure,¹³ the fluctuations of the electron density are given by

$$\rho(z) = \sum a_n \cos(n2\pi z/d)$$

Experimentally we measure the intensity of the diffraction orders so we lose the phase and we do not know the sign of a_n . Because each mesophase exhibits three reflections, there are eight possible combinations of signs for a_n , that is to say, eight possible electron density profiles $\rho(z)$

that we describe as follows: $\rho + - +$ will correspond to the combination where a_1 and a_3 are chosen positive while a_2 is chosen negative.

To choose the physically acceptable one among the eight possible profiles, we calculated the electron density of the different parts of the repeating unit of the polymer by dividing their number of electrons by their lengths measured on CPK models. We found 9.2 e⁻/Å for the skeleton, 6.4 e⁻/Å for the paraffinic spacer, and 9.7 e⁻/Å for the mesogenic groups.

In the case of an orthogonal interdigitated structure (SAd or SBd) [Fig. 6(b)], one must observe a central maximum corresponding to the partly interdigitated mesogenic groups surrounded by two minimums corresponding to the spacers and two secondary maximums corresponding to the polymeric skeleton.⁵

In the case of a double layer tilted smectic structures (SC2 or SF2 or SI2) [Fig. 6(a)], one must observe a central minimum surrounded by two maximums corresponding to the mesogenic cores, two minimums corresponding to the paraffinic spacers, and two maximums corresponding to the polymeric skeleton.⁵

The eight electron density profiles of the ordered smectic structure are represented in Figure 7(a–h). The four electron density profiles (e–h) are incompatible with both SBd and SF2 or SI2 structures because they exhibit minimums for the main chains and maximums for the paraffinic

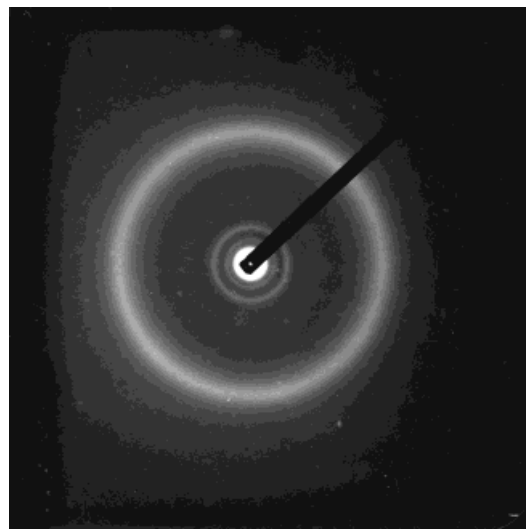


Figure 5 Pinhole camera powder X-ray diagram of the SC2 mesophase of the polymer **pIIIIf** at 120°C showing the three small angle sharp reflections and the wide angle diffuse band.

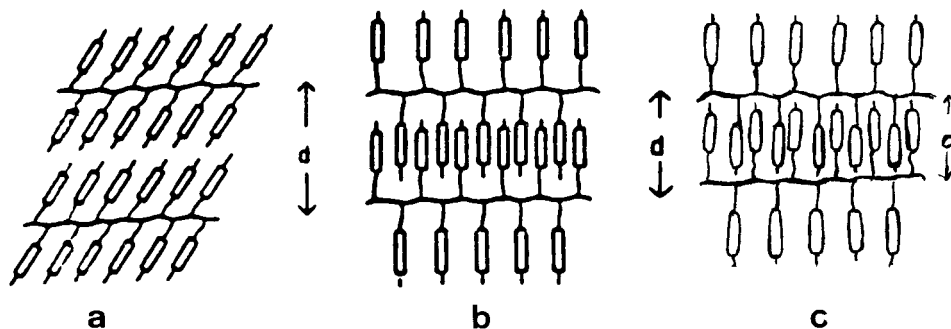


Figure 6 Schematic representation of the different smectic structures: (a) bilayer tilted smectic structures SC2 or SF2 or SI2; (b) interdigitated perpendicular smectic structures SAd or SBd; and (c) monolayer perpendicular smectic structures SA1 or SB1.

spacers. The four electron density profiles (a–d) are incompatible with a SBd structure because they exhibit minimums in the middle of the layers where the mesogenic cores would be partially interdigitated, so the SBd structure must be rejected. On the contrary they are in agreement with an SF2 or SI2 structure because they exhibit

a minimum in the middle of the layer surrounded by maximums at the position of the mesogenic cores, minimums at the position of the paraffinic spacers, and maximums at the position of the polymeric skeleton. To choose the most probable one among the four electron density profiles (a–d), we have to compare the electron density of

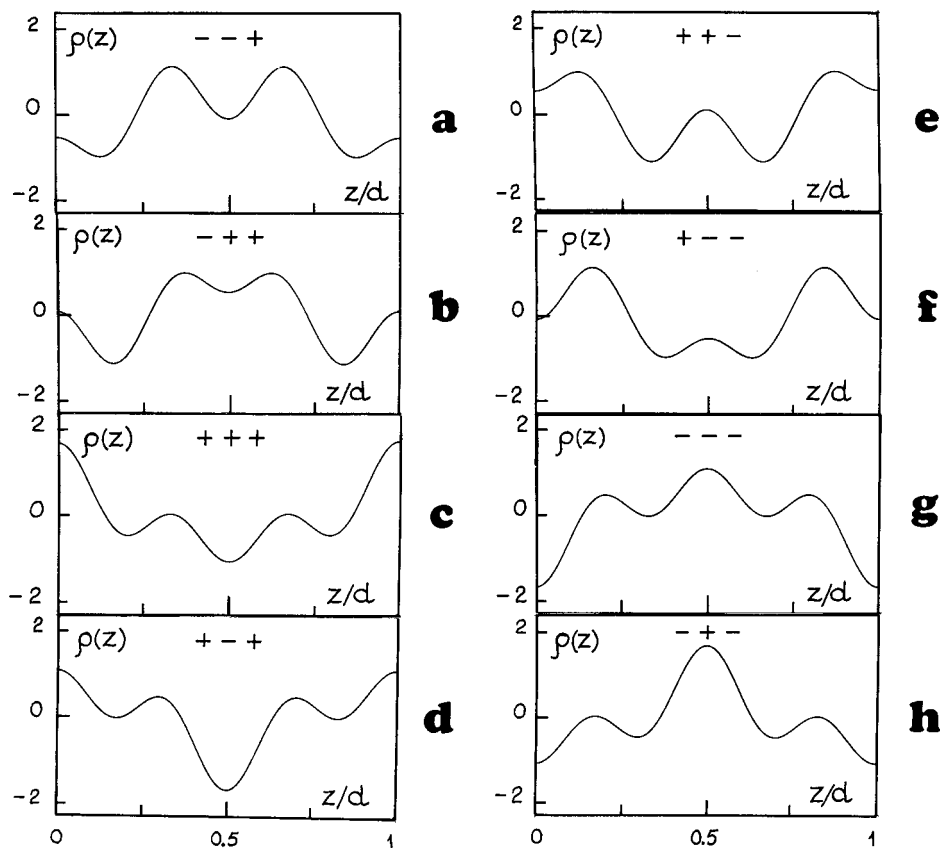


Figure 7 Projections of the electron density profiles corresponding to the eight different sign combinations of a_n for the polymer **pIII f** in the SF2 phase.

the mesogenic cores and the main chain on the one hand, and the 2-methyl-1-butoxy tails and the methylene spacers on the other hand. The biphenyl mesogenic cores exhibit the highest electron density (9.7), so the electron density profiles (c) and (d) can be rejected. Profiles (a) and (b) both exhibit higher maximums for the mesogens than for the main chains and minimums more important for the spacers than for the tails, so they are both in agreement with a double layer tilted smectic phase. The difference of amplitude of the maximums corresponding to the main chains reflects the differences of separation between main chains and spacers. Profile (a) corresponds to an important interpenetration between main chains and spacers, and profile (b) corresponds to a phase separation between main chains and spacers. Because the thermal domain of stability of the ordered smectic phase corresponds to a polymer in the glassy state, the rigidity of the main chains is high and we chose the electron density profile (b) corresponding to $\rho(z) - + +$.

The structure factors of the disordered smectic phase are very similar to those of the ordered one (see X-ray in Experimental) and therefore the electron density profiles are also very similar. They are all incompatible with an interdigitated smectic (SAd) but four of them are in agreement with a double layer tilted smectic SC2. In Figure 8 we only represented the electron density profiles (a) and (b) that exhibit highest maximums for the mesogens. Taking into account the difference of rigidity of the main chains in the two mesophases, for the disordered SC2 phase we can favor the electron density profile (a) corresponding to $\rho(z) - - +$ that corresponds to an important interpenetration between main chains and spacers, in agreement with the small decrease of the layer thickness d of the smectic planes at the transition SF2 SC2 (Table III).

Therefore, we can conclude that polymer pIII_f exhibits, as a function of temperature, two double layer tilted mesophases. The first mesophase is an ordered SF2 phase (the SF2 character results from the thickness at half height of the reflection at wide angles). The second mesophase is a disordered SC2 phase.

Polymer pIII_e: $R_1 = CH_3$, $m = 10$, and $R = CN$

At room temperature, X-ray diagrams exhibit three sharp reflections in the low angle domain. Two reflections correspond to smectic layers with thickness $d = 42.4 \text{ \AA}$; the third one corresponds

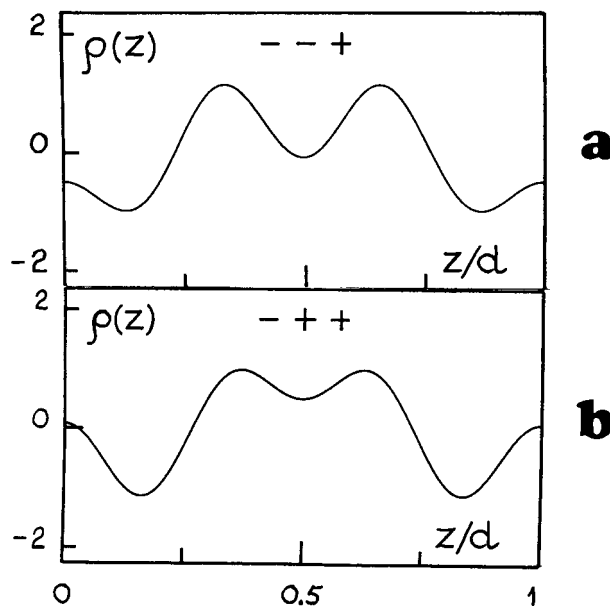


Figure 8 Projections of the electron density profiles corresponding to the most physically acceptable sign combination of a_n for the polymer pIII_f in the SC2 phase.

to smectic layers with thickness $d = 31.8 \text{ \AA}$ and its intensity decreases when the temperature increases and it disappears at 120°C . Figure 9 shows the variation, as a function of temperature, of the ratio of the intensity of the reflections characteristic of the two lamellar systems.

From room temperature to isotropization temperature (165°C), X-ray diagrams exhibit, in the wide angle domain, a large band characteristic of a disordered smectic structure.

The comparison between the thickness d of the lamellae and the length L ($L = 31 \text{ \AA}$) of the repeating unit of the polymer shows that $d = 1.03L$ for the structure that disappears at 120°C . So the structure of that first mesophase is the monolayer perpendicular smectic A1 type [Fig. 6(c)].

For the structure that remains stable until 165°C , $d = 1.37L$. So the structure can be the tilted double layer SC2 type or the perpendicular interdigitated SAd type. Structure SC2 would exhibit a very high tilt angle, $\phi = 46^\circ$, and would follow a perpendicular smectic structure; therefore, the SC2 structure is very improbable. On the contrary, the SAd structure allows a maximum of interactions among mesogenic groups as illustrated by Figure 10.

Therefore, at room temperature, polymer pIII_e exhibits a mixture of two disordered smectic structures SA1 and SAd. When the temperature

Table III Type, Structural Parameters, and Domain of Stability of Mesophases

Polymer	d (Å)	ϕ°	Structure	Stability (°C)
pIIIa	53.0	18.8	SI2	$T < 105$
	53.0	18.8	SC2	105–160
pIIIb	51.8	24.7	SC2	$T < 95$
	59.0	0.0	A2	95–168
pIIIc	56.8	27.4	SF2	$T < 115$
	57.9	25.2	SC2	115–185
pIIId	31.2	0.0	SB1	$T < 98$
	30.3	0.0	SA1	98–163
pIIIe	31.8	0.0	SA1	$T < 120$
	42.4	0.0	SAd	120–165
pIIIf	49.0	15.3	SF2	$T < 95$
	47.8	9.8	SC2	95–182
pIVb	45.8	0.0	SAd	$T < 190$
pIVc	40.0	0.0	SB1	$T < 127$
	40.0	0.0	SA1	127–148

d , thickness of the smectic layers; ϕ , angle of tilt.

increases, the motions of the main chains increase, and to maintain the stability of the smectic structure the interactions between mesogens must be maximum. Such a condition is fulfilled by the SAd structure that remains alone at temperatures higher than 120°C.

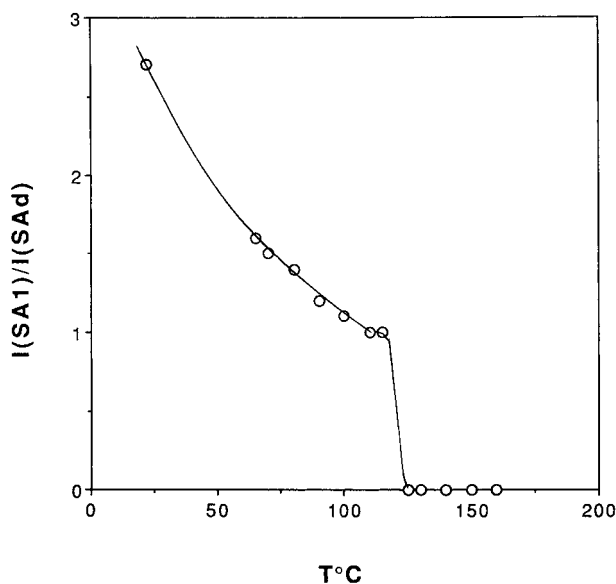


Figure 9 Variation with temperature of the ratio of the intensities of the reflections characteristic of the SA1 and SAd structures of the polymer **pIIIe**.

Factors Governing Nature of Mesophases

The main factors governing the nature, the domain of stability, and the geometrical parameters of the mesophases are the nature of the main chains, the length of the spacers, the nature of the mesogens, and the temperature. We examine these factors successively.

Influence of Nature of Main Chains and Substituents R of Biphenyl Cores

All the polymers are smectic at room temperature and exhibit generally two different smectic phases as a function of temperature (Table III). The type (bilayer, monolayer, or partly interdigitated) of smectic phases is governed by the nature of the main chain, but the substituent R of the biphenyl core determines the detailed lateral organization of the side chains, so the type (A, C, B, F, or I) of the smectic phases. Polyacrylamide polymers exhibit only bilayer smectic phases whose type is determined by the nature of the substituent R of the biphenyl; the smectic phases are SI2 and SC2 for $R = H$, SC2 and SA2 for $R = CN$, and SF2 and SC2 for $R = O-CH_2-CH(CH_3)-C_2H_5$. On the contrary, polymethacrylamide and polystyrylamide polymers exhibit two perpendicular monolayer smectic phases, SB1 and SA1, except for $R = CN$.

When the substituent R of the biphenyl core

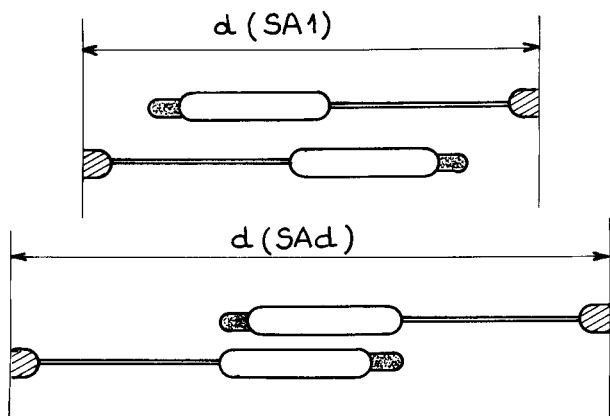


Figure 10 Schematic representation of the structures SA1 and SAd of the polymer **pIIIe**. main chains are the crosshatched sections, spacers are long thin tubes, mesogens are long wide tubes, and CNs are the dot filled sections.

is not polar ($R = H$ or $R = O-CH_2-CH(CH_3)-C_2H_5$) the first mesophase is an ordered smectic phase SI2 or SF2 for polyacrylamide polymers, and SB1 for polymethacrylamide and polystyrylamide polymers. On the contrary, the polar substituent R favors the existence of disordered smectic phases at room temperature: SC2 for polyacrylamides, SA1 and SAd for polymethacrylamides, and SAd for polystyrylamides.

The nature of the substituent R of the biphenyl core also has a big influence on the dynamical properties of comblike liquid-crystalline polymers.^{14,15}

Influence of Length of Spacers

Polymers differing only by the length of the spacers (five methylenes for polymer **pIIIc** and 10 methylenes for polymer **pIIIe**) exhibit the same types of mesophases (SF2 and SC2), but the thickness of the smectic layers is governed by the length of the spacers (Table III).

Influence of Temperature

The increase of temperature at about 100°C generally involves a transition between two smectic phases (Table III). The first mesophase is an ordered smectic phase except for $R = CN$. The phase transition is accompanied or not by a variation of the thickness of the smectic layers, depending upon the nature of the main chains and the substituents R (Table III).

CONCLUDING REMARKS

In this article we described the thermotropic behavior of comblike polymers with polyacrylamide, polymethacrylamide, or polystyrylamide main chains, and spacers of 10 or five methylene groups linked through ester bonds to biphenyl, carbonitrilbiphenyl, or 2-methyl-1-butoxybiphenyl mesogen. All the polymers were smectic at room temperature and exhibited as a function of temperature two different smectic phases, except polymer pIVb with the polystyrylamide main chain and carbonitrilbiphenyl mesogen. But the type of smectic phases was governed by the nature of both the main chain and the substituent R of the biphenyl core. Polyacrylamide polymers exhibited two tilted bilayer mesophases, SF2 or SI2 and SC2⁵ whereas polymethacrylamide and polystyrylamide polymers exhibited two perpendicular monolayer smectic phases, SB1 and SA1, except for $R = CN$ where an SAd phase replaced the SA1 phase (Table III).

It is interesting to compare the thermotropic behavior of comblike polymers with different backbones for two types of biphenyl substituents, a polar one ($R = CN$) and a chiral one ($R = O-CH_2-CH(CH_3)-C_2H_5$). A lot of work has been devoted to the study of the influence of the different fragments (backbone, spacer, interconnecting group between the mesogen and the spacer, mesogen length and constitution) on the thermotropic behavior of side-chain polymers. (See Shibaev and Plate,¹⁶ Percec and Pugh,¹⁷ and Imrie et al.¹⁸ and references therein.) In particular, it has been shown that for fixed backbone, spacer, and mesogen, the nature of the connecting group between the mesogen and spacer does not modify the type of mesophases.¹⁷ So we can compare the polymers described in this article with polymers with other main chains, even if they have different connecting groups between the mesogen and the spacer at the condition that the total number x of carbon atoms of the spacer and the connecting group is the same.

Polymers with carbonitrilbiphenyl mesogens and $x = 11$ but with different main chains [polyacrylates,¹⁹ polyacrylamides,⁵ polymethacrylamides (this work), and polystyrylamides⁸] all exhibit only disordered smectic phases, but the type of the mesophases is governed by the nature of the main chains. Polyacrylates, polymethacrylamides, and polystyrylamides exhibit a SAd phase, but that phase can be the sole one for polystyrylamides, follow a SC2 phase for polyacrylates,

or follow a SA1 phase for polymethacrylamides. On the contrary polyacrylamides exhibit two double layer smectic phases, SC2 and SA2.

Polymers with 2-methyl-1-butoxybiphenyl mesogens and $x = 11$ but differing by the nature of the main chains exhibit a high variety of thermotropic behaviors. Polyacrylates^{19,20} exhibit as a function of temperature a crystalline, a monolayer metastable smectic SC1, and a monolayer smectic SA1 phase; polysiloxanes exhibit a crystalline, a monolayer ordered smectic SF2, and two monolayer disordered smectics SC1 and SA1 phases.²¹ Polyvinylethers exhibit a crystalline, a bilayer disordered smectic SC2, and a monolayer disordered smectic SA1 phases.²² Polyacrylamides and polystyrylamides exhibit an ordered and a disordered smectic phase, but these phases are of the bilayer type (SF2 and SC2) for the polyacrylamides and of the monolayer type (SB1 and SA1) for the polystyrylamides.

So for the two types of substituents of the biphenyl mesogenic cores, the nature of the main chains has a very important influence on the thermotropic behavior of the comblike polymers. Furthermore, polymers with polyacrylamide, polymethacrylamide, and polystyrylamide main chains exhibit a very high smectogenic power that is probably related to the existence of hydrogen bonds resulting from the presence of amide groups in the main chains.

REFERENCES

1. B. Gallot and A. Douy, *Mol. Cryst. Liq. Cryst.*, **153**, 367 (1987).
2. B. Gallot and B. Marchin, *Liq. Cryst.*, **5**, 1719 (1989).
3. B. Gallot and T. Diao, *Liq. Cryst.*, **14**, 947 (1993).
4. B. Gallot and B. Marchin, *Liq. Cryst.*, **5**, 1729 (1989).
5. B. Gallot, F. Monnet, and S. He, *Liq. Cryst.*, **19**, 501 (1995).
6. B. Gallot and F. Monnet, *Eur. Polym. J.*, **32**, 147 (1996).
7. B. Gallot and A. L. Lenclud, *Polymer*, to appear.
8. B. Gallot and L. He, *Macromolecules*, to appear.
9. International Tables for X-ray Crystallography, Vol. 1, The Kynoch Press, Birmingham, 1952.
10. B. Neises and W. Stieglisch, *Angew. Chem. Int. Ed. Engl.*, **17**, 522 (1978).
11. G. Hofle, W. Stieglisch, and H. Vorbruggen, *Angew. Chem. Int. Ed. Engl.*, **17**, 569 (1978).
12. A. De Vries, *Mol. Cryst. Liq. Cryst.*, **131**, 125 (1985).
13. V. A. Gudkov, *Sov. Phys. Crystallogr.*, **29**, 316 (1984).
14. P. Allia, C. Oldano, M. Rajteri, P. Taverna, L. Trossi, F. Monnet, and B. Gallot, *Liq. Cryst.*, **20**, 225 (1996).
15. P. Allia, C. Oldano, P. Taverna, L. Trossi, S. He, and B. Gallot, *Liq. Cryst.*, **22**, 279 (1997).
16. V. P. Shibaev and N. A. Plate, *Pure Appl. Chem.*, **57**, 1589 (1985).
17. C. Percec and C. Pugh, in *Side-Chain Liquid Crystal Polymers*, C. B. McArdle, Ed., Blackie and Sons, Glasgow, UK, 1989, Chap. 3.
18. C. T. Imrie, F. E. Karasz, and G. S. Attard, *Macromolecules*, **26**, 3803 (1993).
19. H. Ringsdorf, C. Urban, W. Knoll, and M. Sawodny, *Makromol. Chem.*, **193**, 1235 (1992).
20. E. Chiellini, G. Galli, F. Cioni, E. Dossi, and B. Gallot, *Mater. Chem.*, **3**, 165 (1993).
21. B. Gallot, G. Galli, E. Dossi, and E. Chiellini, *Liq. Cryst.*, **18**, 463 (1995).
22. E. Chiellini, E. Dossi, G. Galli, R. Solaro, and B. Gallot, *Macromol. Chim. Phys.*, **196**, 3859 (1995).